Radiation-Induced Polymerization of α-Olefines

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In a previous report,(1) the radiation-induced polymerization of 3-methyl butene-1 and 4-methyl pentene-1 was investigated. The polymers obtained were only low-molecular-weight oily oligomers, and a conventional 1, 2 enchainment occurred, in contrast to the high-molecular-weight rearranged structures obtained under low-temperature, conventional cationic polymerization conditions.(2) In this report, the polymerizabilities of isobutene (IB), 3-methyl butene-1 (3MB-1) and 4-methyl pentene-1 (4MP-1) will be compared, particularly considering their sensitivity to traces of water. Moreover, the copolymerization of these α-olefines with sulfur dioxide will be carried out in order to compare the reactivities of these α-olefines.

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Experimental

Isobutene (Tokyo Kasei Co. Ltd.) was introduced through a 50-cm column of KOH into a reservoir kept at −78°C. The reservoir contained CaH_2 and was attached to the vacuum line. After it had stood for two days, the monomer was distilled into a graduated ampoule (normal drying). Alternatively, the monomer was distilled into an ampoule containing Na-K alloy[3] and stored for a week at −78°C. Then, after trap-to-trap distillation onto BaO[4] which had been baked at 300°C for 8 hr at 10^{-5} mmHg before use, the monomer was exhaustively dried by storing it for about three days. The same technique was used for 3MB-1 and 4MP-1 obtained from the Toyo Rayon Co., Ltd. The samples for the copolymerization of α-olefines with SO_2 were prepared by "normal drying." The other experimental techniques were similar to those described in the previous report.[1]

Results and Discussion

The results obtained by the radiation-induced polymerization of α-olefines are summarized in Table 1. The rates of polymerization and the molecular weights of the polymer from IB are much higher than the values obtained for 3MB-1 and 4MP-1; also, they are much more sensitive to traces of water. It is accepted that IB polymerizes by a cationic mechanism[6] and that 3MB-1 and 4MP-1 probably polymerize by a free-radical mechanism.[1] From the infrared and NMR spectra, the structure of all the polymers was estimated to be a conventional 1, 2, repeating one.

TABLE 1. RADIATION-INDUCED POLYMERIZATION OF ISOBUTENE, 3-METHYL BUTENE-1 AND 4-METHYL PENTENE-1 AT −78°C
Dose rate 1.5×10^5 R/hr

Monomer	Method of drying	$G(\text{-M})/100$ eV.	Molecular weight*
Isobutene (IB)	Normal drying	*ca.* 400	80000
	Rigorous drying	*ca.* 250000	6000000
3-Methyl butene-1 (3MB-1)	Normal drying	*ca.* 7	350—700
	Rigorous drying	*ca.* 7	350—700
4-Methyl pentene-1 (4MP-1)	Normal drying	*ca.* 5	420—840
	Rigorous drying	*ca.* 5	420—840

* For polyIB an intrinsic viscosity measurement[5] was used, and for poly3MB-1 and poly4MP-1 a vapor pressure osmometer measurement[1] was used.

Although there have been some reports[7,8] on the radiation-induced copolymerization of α-olefines with SO_2, those of 3MB-1 and 4MP-1 have not yet been reported. The rates of the polymerization (R_p) of α-olefines and SO_2 were very high. All the polymers obtained were white powders and were estimated, from the elementary analysis, to be composed of equal moles of α-olefines and SO_2. The dependence of R_p on the temperature is shown in Fig. 1. The order of the maximum R_p value was IB-SO_2>3MB-1-SO_2>4MP-1-SO_2. The ceiling temperatures of the copolymerization were *ca.* 5°C (IB-SO_2), *ca.* 35°C (3MB-1-SO_2) and *ca.* 50°C (4MP-1-SO_2). Because the copolymers of α-olefines - SO_2 could not be dissolved in normal organic solvents, the structure of the copolymer could not be investigated by means of NMR, but it was estimated that there was less possibility for isomerization polymerization from the determination of the 8.5 μ absorption contributed by the pendant isopropyl group in the infrared spectra measurements.

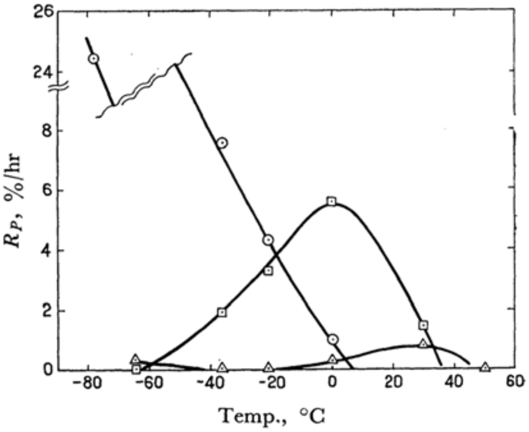

Fig. 1. Rate of copolymerization of α-olefines with SO_2.
Dose rate 9×10^3 r/hr.
α-olefine/SO_2=1 (molar ratio)
⊙ IB-SO_2, ⊡ 3MB-1 - SO_2, △ 4MP-1 - SO_2

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